

RIGOROUS ROUTE TO INTERACTION POTENTIALS FOR REACTIVE MODELS DERIVED FROM CONDENSED PHASE AB INITIO SIMULATIONS

Chris Knight^{1,2} and Gregory A. Voth^{1,2,3}

1. Computing, Environment, and Life Sciences,
Argonne National Laboratory, 9700 South Cass Ave.,
Argonne, IL 60439

2. Computation Institute,
University of Chicago, 5735 South Ellis Avenue,
Chicago, IL 60637

3. Department of Chemistry, James Franck Institute, and
Institute for Biophysical Dynamics,
University of Chicago, 5735 South Ellis Avenue,
Chicago, IL 60637

INTRODUCTION

The number of separate components and interfaces in condensed phase environments complicates the ability to efficiently and accurately simulate chemically reactive processes. The simulation of these reactive processes is not possible with typical molecular mechanics force fields, which assume fixed bonding topologies. Ab initio condensed phase simulations, which naturally account for variable bond topologies, are currently possible, but the computational cost to obtain sufficient statistics is too prohibitive. It would thus be highly advantageous to have a general methodology to develop empirical reactive force fields derived from condensed phase electronic structure calculations. When properly parameterized, these reactive models would reproduce the thermodynamic and dynamic properties of the original calculation, but at a significantly reduced computational cost enabling one to statistically converge physical properties at the required length and time scales. This work will discuss recent developments in force-matching algorithms to construct reactive models derived from condensed phase ab initio simulations.

METHODOLOGY

The modeling of chemical reactions requires a methodology that is capable of a dynamical rearrangement of the bonding topology in response to changes in the environment and intrinsic quantum mechanics of the reaction. To address this challenge, a multistate method [1, 2] is used whereby the system is represented as a linear combination of several possible bonding topologies (diabatic states) that are coupled to one another through the off-diagonal elements of a quantum-like Hamiltonian matrix. The matrix elements are evaluated as relatively simple functions of the coordinates of all particles in the system with the diagonal elements largely evaluated using traditional molecular mechanics forcefields for each distinct bonding topology. The main achievement in this work is the development of

an iterative, linear force-matching algorithm (Figure 1) to define interaction potentials specific to the reactive model as general flexible tabulated functions that are parameterized using Hellman-Feynman forces from condensed phase ab initio simulations.[3] The use of tabulated functions precludes the use of empirical functions that may or may not have been validated and would possibly limit the accuracy of the generated model.

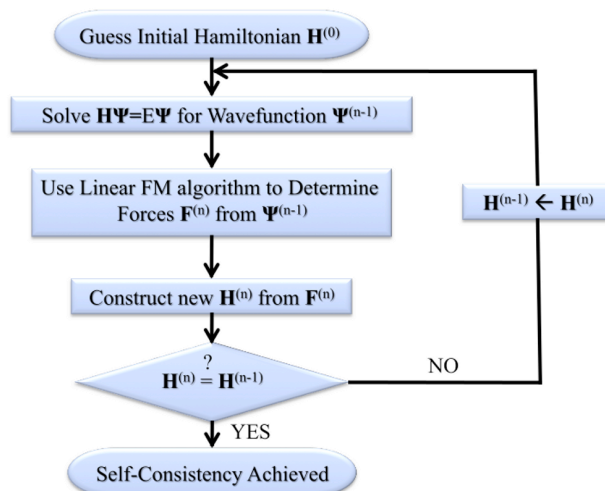


Figure 1: Flow chart outlining the iterative force-matching algorithm used to develop reactive models (Figure 3 of Ref. [3]).

RESULTS

The procedure outlined here was used to develop separate reactive models for the excess proton and hydroxide ion using the results of periodic density functional theory simulations of aqueous systems. For each system, a nonreactive model was first constructed to serve as the underlying molecular mechanics forcefield for the diagonal elements of the multistate Hamiltonian matrix. Using the algorithm outline in Figure 1, the reactive portions of each model were parameterized. The calculated thermodynamic and dynamic properties of the models for both charged defects were found to reproduce the results of the computationally more expensive ab initio molecular dynamics simulations. The high fidelity of these models to ab initio simulations will enable the accurate modeling of chemical reactions in condensed phase systems at length and time scales currently inaccessible to ab initio simulation methodologies.

ACKNOWLEDGMENTS

This work was supported in part through the National Science Foundation (CHE-1214087). We also acknowledge support from the U.S. Department of Energy under Contract DE-AC02-06CH11357 and an Argonne National Laboratory Computational Science Postdoctoral Fellowship to C.K. We also acknowledge support from the Department of Defense Multidisciplinary University Research Initiative through

the Army Research Office (W911NF-10-1-0520). The computations in this work were supported in part by a grant of computer time from the DOD High Performance Computing Modernization Program at the NAVY, Engineer Research and Development Center (ERDC), and Air Force Research Laboratory (AFRL) DOD Supercomputing Resource Centers. This research was also supported in part by the National Science Foundation Teragrid computing resources provided by the Texas Advanced Computing Center under Grant Number TG-MCA94P017. An award of computer time was provided by the Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program. This research used resources of the Argonne Leadership Computing

Facility at Argonne National Laboratory, which is supported by the Office of Science of the U.S. Department of Energy under contract DE-AC02-06CH11357.

REFERENCES

1. Swanson, J. M. J.; Maupin, C. M.; Chen, H.; Petersen, M. K.; Xu, J.; Wu, Y.; Voth, G. A., *J. Phys. Chem. B*, **111**(17), 4300-4314 (2007).
2. Knight, C.; Voth, G. A., *Acc. Chem. Res.*, **45**(1), 101-109 (2012).
3. Knight, C.; Lindberg, G.; Voth, G. A., *J. Chem. Phys.*, **137**(22), 22A525 (2012) DOI=10.1063/1.4743958.